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[US/US]; 167 McKnight Road, Apartment 105, Saint Paul,  
MN 55119 (US).

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(74) Agents: **LOWN, Jean, A.** et al.; Office of Intellectual  
Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-  
3427 (US).

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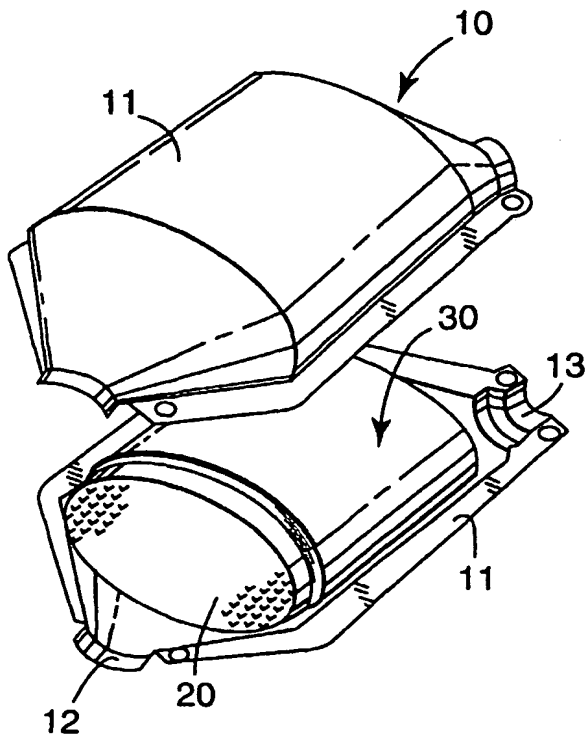
(71) Applicant (for all designated States except US): **3M IN-  
NOVATIVE PROPERTIES COMPANY** [US/US]; 3M  
Center, Post Office Box 33427, Saint Paul, MN 55133-  
3427 (US).

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(54) Title: COMPOSITIONS CONTAINING BIOSOLUBLE INORGANIC FIBERS AND MICACEOUS BINDERS



(57) Abstract: Compositions that include a mixture of  
biosoluble inorganic fibers and a micaceous binder are  
described. The compositions can be prepared free of  
refractory ceramic fibers that are respirable but durable in  
a physiological medium. The compositions are typically  
in the form of a sheet material or a paste and can be used,  
for example, as a protective packing material around the  
pollution control element or as an insulating material in  
the end cone region in a pollution control device. Sheet  
materials formed from the compositions have an area of a  
X-Y plane that decrease less than about 6 percent when  
heated to about 900°C.



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## COMPOSITIONS CONTAINING BIOSOLUBLE INORGANIC FIBERS AND MICACEOUS BINDERS

### Field of the Invention

5           This invention relates to compositions that can be used, for example, as a fire barrier, as a heat barrier such as an insulating material, or as a protective packing material. More specifically, this invention relates to compositions that include a mixture of biosoluble inorganic fibers and a micaceous binder.

### Background of the Invention

10           Pollution control devices are used on motor vehicles to reduce atmospheric pollution. Two types of devices are currently in widespread use: catalytic converters and diesel particulate filters or traps. Catalytic converters contain one or more catalysts, which are typically coated onto a substrate in the form of a monolithic  
15           structure. The monolithic structures are typically ceramic, although metal monoliths have been used. The catalyst(s) oxidize carbon monoxide and hydrocarbons, reduce the oxides of nitrogen in exhaust gases, or a combination thereof. Diesel particulate filters or traps typically are in the form of wall flow filters that have honeycombed monolithic structures made from porous crystalline ceramic materials. In the current  
20           state-of-the-art construction of these pollution control devices, the monolithic structure of each type is enclosed within a housing.

          A typical monolithic structure generally has relatively thin walls to provide a large amount of surface area. Consequently, the structure is fragile and susceptible to breakage. The typical monolithic structure formed from ceramic material tends to have  
25           a coefficient of thermal expansion that is an order of magnitude less than the metal (usually stainless steel) housing in which it might be contained. Protective packing materials such as ceramic mats or paste materials are typically packed between the ceramic monolith and the metal housing to avoid damage to the monolith from road shock and vibration, to compensate for the thermal expansion difference, and to prevent  
30           exhaust gases from passing between the monolith and the metal housing. The process of placing or inserting the protective packing material is referred to as "canning" and includes such processes as injecting a paste into a gap between the monolith and the

metal housing, or wrapping a sheet material (i.e., mounting mat) around the monolith and inserting the wrapped monolith into the housing.

Typically, the compositions used to form conventional protective packing materials include refractory ceramic fibers that provide properties such as high temperature durability, good handling, resiliency, flexibility, and strength. An intumescent material can also be included that enables the protective packing materials to volumetrically expand at elevated temperatures. Such expansion helps to hold the monolith in place during use. Ceramic sheet materials, ceramic pastes, and intumescent sheet materials useful for mounting the monolith in the housing of a pollution control device are described in, for example, U.S. Pat. Nos. 3,916,057 (Hatch et al.), 4,305,992 (Langer et al.), 4,385,135 (Langer et al.), 5,254,410 (Langer et al.), and 5,242,871 (Hashimoto et al.).

### **Summary of the Invention**

Compositions are provided that can be used, for example, as a fire barrier, as a protective packing material around the monolithic structure in a fuel cell or in a pollution control device, or as a heat barrier such as an insulating material positioned in the end cone regions of a pollution control device. In particular, the compositions include a micaceous binder and biosoluble inorganic fibers. The compositions can be prepared free of refractory ceramic fibers that are respirable but durable in a physiological medium.

One aspect of the invention provides a composition that includes a micaceous binder in an amount of about 5 to about 80 weight percent and biosoluble inorganic fibers in an amount of about 5 to about 90 weight percent on a dry weight basis. The compositions can also optionally include intumescent materials, non-respirable inorganic fibers, a polymeric binder, a polymeric fiber, or a combination thereof. The compositions can be provided, for example, in the form of a sheet material or in the form of a paste.

Another aspect of the invention provides a pollution control device that includes a housing, a pollution control element disposed in the housing, and a protective packing material that is disposed in a gap between at least a portion of the housing and the pollution control element. The protective packing material, which is typically in the form of a paste or a sheet material, includes a micaceous binder and biosoluble

inorganic fibers. The protective packing material can protect the fragile pollution control element from damage due to road shock and vibration, can compensate for thermal expansion differences between the pollution control element and the housing, can prevent exhaust gases from by passing the pollution control element, or a combination thereof.

Yet another aspect of the invention provides a pollution control device that includes a housing and heat barrier (i.e., insulating material) disposed in the housing. The heat barrier includes a micaceous binder and biosoluble inorganic fibers. The heat barrier is typically located in an end cone region of the pollution control device and can be in the form of a sheet material or a paste.

The invention also provides a method of making a sheet material. The method includes forming a slurry that contains a micaceous binder in an amount of about 5 to about 80 weight percent on a dry weight basis and biosoluble inorganic fibers in an amount of about 5 to about 90 weight percent on a dry weight basis, adding a coagulating agent to form a coagulated slurry, and removing water from the coagulated slurry to form a sheet material.

Yet another aspect of the invention provides a method of making a pollution control device that includes a pollution control element, a protective packing material, and a pollution control element. The method includes preparing a protective packing material that contains a micaceous binder and biosoluble inorganic fibers, placing the pollution control element in the housing, and positioning the protective packing material between at least a portion of the housing and the pollution control element. The protective packing material can be in the form of a sheet material or a paste.

Another aspect of the invention provides a sheet material that includes a micaceous binder and biosoluble inorganic fibers. When the sheet material is heated to about 900 °C or to the temperatures typically encountered in a pollution control device, the area of the sheet in the X-Y plane shrinks less than about 6 percent.

The above summary of the present invention is not intended to describe each disclosed embodiment or every implementation of the present invention. The Figures and the detailed description that follow more particularly exemplify these embodiments.

### **Brief Description of the Drawings**

The invention can be more completely understood in consideration of the following detailed description of various embodiments of the invention in connection with the accompanying drawings, in which:

5        Figure 1 is a perspective view of a catalytic converter incorporating an embodiment of the present invention and shown in disassembled relation.

Figure 2 is a longitudinal central section through a diesel particulate filter incorporating an embodiment of the present invention.

10       Figure 3 is a plot of pressure versus temperature data obtained from a Real Condition Fixture Test of a sheet material embodiment of the present invention.

Figure 4 is a plot of pressure versus temperature data obtained from a Real Condition Fixture Test of another sheet material embodiment of the present invention.

15       While the invention is amenable to various modifications and alternative forms, specifics thereof have been shown by way of example in the drawings and will be described in detail. It should be understood, however, that the intention is not to limit the invention to the particular embodiments described. On the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention.

### **Detailed Description of the Invention**

20       Compositions are provided that can be used as heat barriers (i.e., insulating materials), as fire barriers, or as protective packing materials. In particular, the compositions include a micaceous binder and biosoluble inorganic fibers. The compositions can be, for example, in the form of a sheet material or a paste. The  
25       compositions are typically prepared free of refractory ceramic fibers that are respirable but durable in a physiological medium.

The compositions of the invention can be used as heat barriers, fire barriers, or a combination thereof. For example, the compositions can be placed around pipes, heating devices, or structural elements such as building supports.

30       In another example, the compositions can be used in pollution control devices as an insulating material. For example, the compositions can be positioned in the inlet or outlet regions (i.e., the end cone regions) of a pollution control device. The compositions can function to insulate the rest of the exhaust system as well as the

engine from the temperatures encountered in the pollution control device. When the composition is in the form of a sheet material, the sheet material can be cut and shaped to conform to the shape of the end cone region of the pollution control device.

Alternatively, the composition can be placed in a mold having the desired final shape.

5           The compositions can also be used to provide a protective packing material.

For example, the compositions can be used as a protective packing material around the monolithic structure of a fuel cell. In another example, the compositions can be used as a protective material between the fragile monolith structure of the pollution control element and the housing of a pollution control device. That is, the compositions can be  
10       disposed in the gap between the monolith of the pollution control element and the housing of pollution control device. The compositions can be, for example, in the form of a paste or sheet material. In one embodiment, the compositions are in the form of a sheet material such as a mounting mat. At least a portion of the monolith pollution control element is wrapped with the sheet material. The wrapped pollution control  
15       element is placed in the housing of the pollution control device. In another embodiment, the compositions are in the form of a paste that can be injected into the pollution control device between at least a portion of the fragile monolith structure of the pollution control element and the housing.

          An illustrative example of a pollution control device in the form of catalytic  
20       converter 10 is shown in Figure 1. The catalytic converter 10 generally includes a housing 11 surrounding a catalytic converter element 20. The housing 11 has inlet 12 and outlet 13 through which a flow of exhaust gases flows into and out of catalytic converter 10, respectively. The housing 11, which is also referred to as a can or a casing, can be made from suitable materials known in the art for such use. Typically,  
25       housing 11 includes one or more metals, metal alloys, and/or intermetallic compositions (hereinafter collectively "metals"). For example, the housing 11 can be stainless steel.

          Suitable catalytic converter elements, also referred to as monoliths, are known in the art and include those made of metal, ceramic, or other materials. A variety of  
30       ceramic catalytic converter elements are commercially available from a variety of sources. For example, a honeycomb ceramic catalytic converter element is marketed under the trade designation "CELCOR" by Corning Inc., and another is marketed under

the trade designation "HONEYCERAM" by NGK Insulated Ltd. Metal catalytic converter elements are commercially available from Behr GmbH and Co. of Germany.

One or more catalyst materials can be coated onto catalytic converter element 20 in accordance with conventional practices. The catalysts used in the catalytic converter element 20 are typically one or more metals (e.g., ruthenium, osmium, rhodium, iridium, nickel, palladium, and platinum) and/or metal oxides (e.g., vanadium pentoxide and titanium dioxide). Most commonly, these catalysts function to oxidize or otherwise eliminate exhaust contaminants such as carbon monoxide and hydrocarbons. Such catalysts also can function to help reduce the amount of oxides of nitrogen in engine exhaust.

To provide a large amount of surface area, embodiments of catalytic converter element 20 generally have very thin walls. The thin walls can cause the catalytic converter element 20 to be fragile and susceptible to breakage. Additionally, in some embodiments, the catalytic converter element 20 can have a coefficient of thermal expansion about an order of magnitude less than that of housing 11. This is particularly the case when housing 11 includes a metal (usually stainless steel) and element 20 is a ceramic. The difference in thermal properties can subject catalytic converter element 20 to a risk of damage with changes in temperature. Mounting mat or sheet material 30, disposed between housing 11 and element 20, helps protect element 20 from damage due to road shock and vibration and/or the thermal expansion difference. Mounting mat or sheet material 30 also helps prevent exhaust gasses from passing between the element 20 and the metal housing 11.

Figure 2 shows a representative example of a pollution control device in the form of diesel particulate filter 40. The diesel particulate filter or trap 40 is a wall flow filter that includes a honeycombed monolithic structure 42 having a bundle of tubes. Such diesel particulate filter elements are commercially available from a number of sources including, for example, Corning Inc. of Corning, N.Y., and NGK Insulator Ltd. of Nagoya, Japan. Useful diesel particulate filter elements are discussed in "Cellular Ceramic Diesel Particulate Filter," Howitt et al., Paper No. 810114, SAE Technical Paper Series, 1981.

A catalyst may be coated onto the monolithic structure 42 mounted in the diesel particulate filter 40. The diesel particulate filter 40 includes a housing 44 having inlet 46 and outlet 48. Housing 44 surrounds particulate filter element 42 (also referred to



as a monolith or monolithic structure). Mounting mat or sheet material 50 is disposed between the filter element 42 and the metal housing 44 and provides the same benefits as mounting sheet 30 of Figure 1.

5 Relatively small refractory ceramic fibers, i.e., those having an average diameter of less than about 5 to 6 micrometers and length greater than about 5 micrometers, have been an important component of known mounting mat compositions for pollution control devices. However, fibers in this size range can be respirable and are often durable in physiological fluids, in particular, lung fluids. Thus, protective  
10 packing material compositions lacking durable, respirable, refractory ceramic fibers are desired. It has been a significant engineering challenge, however, to make acceptable sheet materials, such as mounting mats for pollution control devices, without the durable, respirable, refractory ceramic fibers.

As used herein, the term "fiber" refers to materials having a length that is greater than the width. In some embodiments, the length is at least 10 times, at least  
15 100 times, or at least 1000 times the diameter.

As used herein, the term "respirable" refers to fibers that can be inhaled by an animal into the lungs of the animal. Typically, respirable fibers have an average diameter less than about 5 micrometers. In some embodiments, respirable fibers have an average diameter less than about 3 micrometers. Conversely, as used herein, the  
20 term "non-respirable" refers to fibers that cannot be inhaled by an animal into the lungs of the animal. Typically, non-respirable fibers have an average diameter of at least about 3 micrometers. In some embodiments, non-respirable fibers have an average diameter of at least about 5 micrometers.

One aspect of the invention provides compositions that include biosoluble  
25 inorganic fibers in an amount of about 5 to about 90 weight percent on a dry weight basis and micaceous binders in an amount of about 5 to about 80 weight percent on a dry weight basis. The compositions can also optionally include intumescent materials, non-respirable inorganic fibers, polymeric binders, polymeric fibers, or a combination thereof. The composition can be prepared free of refractory ceramic fibers that are  
30 respirable but durable in a physiological medium.

In some embodiments, the combination of a micaceous binder and biosoluble inorganic fiber can be substituted for all or a portion of the durable refractory fiber content, both respirable and non-respirable, of conventional sheet materials used in

various applications such as pollution control devices. In particular, the combination of biosoluble fibers and micaceous binders can be advantageously substituted for the durable, refractory ceramic fibers that are respirable in size.

As used herein, "biosoluble inorganic oxides fibers" refer to inorganic fibers that are decomposable in a physiological medium or a simulated physiological medium. Physiological medium refers to, but is not limited to, those bodily fluids typically found in the respiratory tract such as, for example, the lungs of animals or humans. As used herein, "durable" refers to inorganic fibers that are not biosoluble.

Biosolubility can be estimated by observing the effects of direct implantation of the inorganic fibers in test animals or by examination of animals or humans that have been exposed to inorganic fibers. Biosolubility can also be estimated by measuring the solubility of the fibers as a function of time in simulated physiological medium such as saline solutions, buffered saline solutions, or the like. One such method of determining solubility is described in U.S. Patent No. 5,874,375 (Zoit et al.).

Typically, biosoluble inorganic fibers are soluble or substantially soluble in a physiological medium within about 1 year. As used herein, the term "substantially soluble" refers to inorganic fibers that are at least about 75 weight percent dissolved. In some embodiments, at least about 50 percent of the inorganic fibers are soluble in a physiological medium within about six months. In other embodiments, at least about 50 percent of the fibers are soluble in a physiological fluid within about three months. In still other embodiments, at least about 50 percent of the inorganic fibers are soluble in a physiological fluid within at least about 40 days. For example, the inorganic fibers can be certified by the Fraunhofer Institut as passing the tests for the biopersistence of high temperature insulation fibers in rats after intratracheal instillation (i.e., the fibers have a halftime less than 40 days).

Yet another approach to estimating the biosolubility of inorganic fibers is based on the composition of the inorganic fibers. For example, Germany classifies respirable inorganic oxide fibers based on a carcinogenicity index (KI value). The KI value is calculated by a summation of the weight percentages of alkaline and alkaline-earth oxides and subtraction of two times the weight percent of aluminum oxide in inorganic oxide fibers. Inorganic fibers that are biosoluble typically have a KI value of about 40 or greater.

The biosoluble inorganic fibers typically include inorganic oxides such as, for example,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Li}_2\text{O}$ , and  $\text{BaO}$ , or combinations thereof with silica. Other metal oxides or other ceramic constituents can be included in the biosoluble inorganic fibers even though these constituents, by themselves, lack the  
5 desired solubility but are present in low enough quantities such that the fibers, as a whole, are still decomposable in a physiological medium. Such metal oxides include, for example,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{B}_2\text{O}_3$ , and iron oxides. The biosoluble inorganic fibers can also include metallic components in amounts such that the fibers are decomposable in a physiological medium or simulated physiological medium.

10 In one embodiment, the biosoluble inorganic fibers include oxides of silica, magnesium, and calcium. These types of fibers are typically referred to as calcium magnesium silicate fibers. The calcium magnesium silicate fibers usually contain less than about 10 weight percent aluminum oxide. In some embodiments, the fibers include from about 45 to about 90 weight percent  $\text{SiO}_2$ , up to about 45 weight percent  
15  $\text{CaO}$ , up to about 35 weight percent  $\text{MgO}$ , and less than about 10 weight percent  $\text{Al}_2\text{O}_3$ . For example, the fibers can contain about 55 to about 75 weight percent  $\text{SiO}_2$ , about 25 to about 45 weight percent  $\text{CaO}$ , about 1 to about 10 weight percent  $\text{MgO}$ , and less than about 5 weight percent  $\text{Al}_2\text{O}_3$ .

Suitable biosoluble inorganic oxides fibers are described in U.S. Patent Nos.  
20 5,332,699 (Olds et al.); 5,585,312 (TenEyck et al.); 5,714,421 (Olds et al.); 5,874,375 (Zoitaz et al.); and European Patent Application 02078103.5 filed on July 31, 2002. Various methods can be used to form biosoluble inorganic fibers including, but not limited to, sol gel formation, crystal growing processes, and melt forming techniques such as spinning or blowing.

25 Biosoluble fibers are commercially available from Unifrax Corporation (Niagara Falls, NY) under the trade designation "INSULFRAX". Other biosoluble fibers are sold by Thermal Ceramics (located in Augusta, GA) under the trade designation "SUPERWOOL." For example, SUPERWOOL 607 contains 60 to 70 weight percent  $\text{SiO}_2$ , 25 to 35 weight percent  $\text{CaO}$ , 4 to 7 weight percent  $\text{MgO}$ , and a  
30 trace amount of  $\text{Al}_2\text{O}_3$ . SUPERWOOL 607 MAX can be used at a slightly higher temperature and contains 60 to 70 weight percent  $\text{SiO}_2$ , 16 to 22 weight percent  $\text{CaO}$ , 12 to 19 weight percent  $\text{MgO}$ , and a trace amount of  $\text{Al}_2\text{O}_3$ .

Suitable biosoluble inorganic fibers can have a wide range of average diameters and average lengths. Biosoluble inorganic fibers are commercially available that have an average fiber diameter in the range of about 0.05 micrometers to about 15 micrometers. In some embodiments, the biosoluble inorganic fibers have average fiber diameters in the range of about 0.1 micrometers to about 5 micrometers. As the average diameter of the biosoluble inorganic fibers decreases, an increased amount of the fiber can be incorporated into a given volume of the sheet material resulting in better entrapment of the micaceous binder. Sheet materials prepared having a higher density of fibers tend to have better resiliency and flexibility.

The biosoluble inorganic fibers typically have an average fiber length in the range of about 0.1 centimeters to about 3 centimeters. Generally, the length of the biosoluble inorganic fibers is not critical as any selected fiber(s) can be broken down into smaller lengths during the manufacturing process, if desired.

As used herein, the phrase "micaceous mineral" refers to a family of minerals that can be split or otherwise separated into planar sheets or platelets. Micaceous minerals include, but are not limited to, expanded vermiculite, unexpanded vermiculite, and mica. Micaceous minerals typically have an average aspect ratio (i.e., the length of a particle divided by its thickness) that is greater than about 3.

As used herein, "micaceous binder" refers to one or more micaceous minerals that can be wetted and then dried to form a cohesive body that is self-supporting. As used herein, "self-supporting" refers to a micaceous binder that can be formed into a 5 cm x 5 cm x 3 mm sheet containing no other materials such that the dried sheet can be held horizontally at any edge for at least 5 minutes at 25 °C and up to 50 percent relative humidity without crumbling or otherwise falling apart.

Micaceous binders include micaceous minerals that typically have a particle size less than about 150 micrometers (e.g., the micaceous binder contains micaceous minerals that can pass through a 100 mesh screen). In some embodiments, the micaceous binder contains micaceous minerals having a size less than about 150 micrometers and having an average aspect ratio of greater than about 8 or greater than about 10.

Suitable micaceous binders can include micaceous minerals that have been crushed. As used herein, "crushed" refers to micaceous minerals that have been processed in any suitable manner that reduces the average particle size. Methods of

crushing include, but are not limited to, mechanical shearing of a dilute or concentrated slurry, milling, air impact, and rolling.

Other methods can be used alone or in combination with crushing to reduce the particle size. For example, thermal or chemical methods can be used to expand or  
5 expand plus exfoliate the micaceous minerals. Expanded vermiculite can be sheared or otherwise processed in water to produce an aqueous dispersion of delaminated vermiculite particles or platelets. Shearing can be adequately performed, for example, using a high shear mixer such as a blender.

The micaceous binder can be non-intumescent, intumescent, or a combination  
10 thereof. As used herein, "non-intumescent" refers to material that exhibits less than about 10 percent free expansion in thickness when heated to temperatures of about 800 °C to about 900 °C. Free expansion refers to the amount of expansion in the Z-axis that the material undergoes when heated without constraints. As used herein, "intumescent" refers to a material that can exhibit at least about 10 percent free expansion in thickness  
15 under the same conditions.

In some embodiments, the micaceous binder includes processed vermiculites (i.e., vermiculate that has been expanded, delaminated, and crushed). Processed vermiculite is typically non-intumescent. In other embodiments, the micaceous binder includes vermiculite that has not been expanded and delaminated or that has been only  
20 partially expanded and delaminated. Such materials tend to be intumescent.

Suitable micaceous binders are commercially available from W. R. Grace & Company, and include a delaminated vermiculite powder (under the trade designation "VFPS") and an aqueous dispersion of chemically exfoliated vermiculite (under the trade designation "MICROLITE). Also, expanded vermiculite flakes are available  
25 from W.R. Grace and Company (under the trade designation "ZONELITE #5") that can be reduced in particle size to form a micaceous binder.

In some embodiments, the compositions of the invention are in the form of a sheet material. Biosoluble inorganic fibers by themselves are not a practical substitute for durable, refractory ceramic fibers used in conventional sheet materials. For  
30 example, biosoluble inorganic fibers tend to exhibit excessive shrinkage when subjected to the temperature extremes encountered during use of a typical pollution control device. Excessive mounting mat or sheet material shrinkage could result in the fragile monolith pollution control element being loosely held inside the housing of the

pollution control device. A loosely held monolith structure can be easily damaged, for example, from a physical shock.

Sheet materials (i.e., mounting mats) prepared by direct substitution of the durable, refractory ceramic fibers in conventional mounting mats with biosoluble inorganic fibers may have adequate initial, cold holding performance (i.e., such mounting mats can hold a pollution control element in a metal housing at room temperature prior to experiencing an elevated temperature). However, such sheet materials tend to shrink and thereby fail to retain the desired holding capabilities when heated to the actual use temperatures.

The present invention provides a sheet material that includes a micaceous binder and biosoluble inorganic fibers. The sheet materials of the present invention typically shrink less than about 6 percent upon heating to about 900 °C or the temperatures typically encountered during use of a pollution control device. Surprisingly, the shrinkage problem burdening biosoluble inorganic fibers can be substantially avoided when biosoluble inorganic fibers and micaceous binder are used in combination.

Sheet materials containing the combination of micaceous binder and biosoluble inorganic fibers can be used at operating temperatures well above temperature suitable for a sheet material containing biosoluble inorganic fibers without the micaceous binder. The sheet materials can typically be used at temperatures up to about 800 °C. In some embodiments, the sheet material can be used at temperatures up to about 850 °C, up to about 900 °C, or up to about 950 °C.

The amount of biosoluble inorganic fiber and micaceous binder included in the sheet materials of the invention can vary within a wide range. The biosoluble inorganic fibers are typically present in an amount to ensure that the resultant mounting mat or sheet material has the desired degree of flexibility and handling characteristics. Flexible sheet materials facilitate wrapping the sheet material around a pollution control element during the canning process. However, if too much biosoluble inorganic fiber is used, the mounting mat or sheet material may shrink more than is desired upon heating.

Balancing these concerns, the compositions of the invention typically contain up to about 90 weight percent of the biosoluble inorganic fibers on a dry weight basis. In some embodiment, the compositions include up to about 85 percent, up to about 80

percent, up to about 60 weight percent, up to about 40 weight percent, or up to about 30 weight percent of the biosoluble fibers on a dry weight basis.

5 The dry weight of the composition refers to the weight of the solids in the composition. Thus, when the composition is in the form of a sheet material, the dry weight refers to the final weight after drying the sheet material to remove all water and solvents. When the composition is in the form of a slurry or paste, the dry weight is the total weight minus the weight of water and any other solvents. That is, the dry basis weight includes the weight of the biosoluble fibers, the micaceous binder, and other solids such as the solids from polymeric binder, polymeric fiber, intumescent materials, non-respirable inorganic fibers, etc. The dry basis weight typically does not include other materials that can result in some solids in miniscule amounts (e.g., less than about 10 0.5 weight percent of the dry basis weight of the mat) such as defoaming agents, coagulating agents, and surfactants. Large portions of these materials tend to remain in solution and are drained with the water during the process of making the sheet materials.

15 The compositions typically includes at least about 5 weight percent biosoluble inorganic fibers on a dry weight basis. In some embodiments, the compositions includes at least about 10 weight percent or at least about 15 weight percent of the biosoluble inorganic fibers on a dry weight basis.

20 The biosoluble inorganic fibers are typically included in the composition in an amount in the range of about 5 to about 90 weight percent, in the range of about 5 to about 85 weight percent, in the range of about 5 to about 80 weight percent, in the range of about 10 to about 60 weight percent, in the range of about 15 to about 40 weight percent, or in the range of about 15 to about 30 weight percent on a dry weight basis.

25 The compositions typically include up to about 80 weight percent micaceous binder on a dry weight basis. In some embodiments, the compositions include up to about 60 percent, up to about 50 percent, or up to about 45 weight percent of the micaceous binder on a dry weight basis.

30 The compositions typically include at least about 5 weight percent micaceous binder based on the total dry weight of the composition. In some embodiments, the composition includes at least about 10 weight percent, or at least about 15 weight percent micaceous binder on a dry weight basis.

The micaceous binder is typically present in the composition in an amount in the range of about 5 to about 80 weight percent, in the range of about 10 to about 60 weight percent, in the range of about 15 to about 50 weight percent, or in the range of about 15 to about 45 weight percent on a dry weight basis.

5 When sheet materials are formed from the compositions described above using expanded, delaminated, and crushed vermiculite, the resultant sheet materials are substantially non-intumescent. Using unexpanded vermiculite dust can result in a greater amount of free expansion along the Z-axis, depending upon the amount of unexpanded vermiculite used. Whether prepared using a non-intumescent or an  
10 intumescent micaceous binder, the sheet materials typically exhibit shrinkage of less than about 6 percent in the X-Y plane of the sheet. In some embodiments, the shrinkage in the X-Y plane is less than about 5 percent. A formula for determining shrinkage is provided below.

The compositions can optionally include non-respirable inorganic fibers. The  
15 non-respirable fibers can be biosoluble or can be durable. Non-respirable inorganic fibers that are durable can include, for example, ceramic materials such as ceramic oxides, ceramic nitrides, glass materials, or a combination thereof. The term "glass", as used herein, refers to an amorphous, inorganic material such as an oxide having a diffuse x-ray diffraction pattern at least substantially without definite lines or other  
20 indicia of a crystalline phase.

If the fibers are longer than desired when obtained from a desired source, the fibers can be chopped, cut, or otherwise processed to reduce the fiber length to a desired length. The fibers typically have an average length in the range of about 0.1 cm to about 1 cm.

25 The amount of non-respirable inorganic fiber incorporated into the composition can vary over a wide range. As a general guideline, compositions of the present invention can include up to about 15 weight percent non-respirable inorganic fibers on a dry weight basis. In some embodiments, the compositions contains up to about 10 weight percent, up to about 5 weight percent, or up to about 3 weight percent of the  
30 non-respirable inorganic fibers on a dry weight basis.

The compositions of the present invention can also include intumescent, inorganic materials having an average particle size greater than about 300 micrometers. In some embodiments, the intumescent material is micaceous and has a particle size



greater than 150 micrometers (i.e., the particles do not pass through a 100 mesh screen). That is, when the intumescent material is micaceous, any particles smaller than about 150 micrometers are considered a micaceous binder.

5 A composition containing an intumescent material can expand when heated and can typically exert sufficient pressure between a pollution control element and the housing of the pollution control device to form a supportive, protective seal. In some embodiments, such a composition can remain resiliently compressible such that the pollution control element is cushioned against physical shocks.

10 Examples of suitable intumescent, inorganic materials having an average particle size greater than about 300 micrometers include unexpanded vermiculite, vermiculite ore, hydrobiotite, water swellable synthetic tetrasilicic fluorine type mica described in U.S. Pat. No. 3,001,571 (Hatch), alkali metal silicate granules as described in U.S. Pat. No. 4,521,333 (Graham et al.), expandable graphite, combinations of these, and the like. Other suitable intumescent materials include, for example, granules sold  
15 by 3M (St. Paul, MN) under the trade designation "EXPANTROL 4BW". Some of these intumescent materials can exhibit more than 10 percent free expansion in thickness when heated to temperatures above about 200 °C or about 300 °C. Additionally, some of these intumescent materials can exhibit more than about 50 percent free expansion when heated.

20 The amount of intumescent material having an average particle size greater than about 300 micrometers included in the compositions can vary over a wide range. If too little intumescent material is present, the composition may expand less than desired. For example, when such a composition is in the form of a mounting mat in a pollution control device, the mounting mat may not support the monolith adequately during use.  
25 On the other hand, if too much intumescent material is used, the composition may expand too much when heated. For example, when the composition is in the form of a mounting mat, the pressure against the pollution control element may be too high, perhaps damaging the pollution control element.

30 Balancing these concerns, compositions generally include up to about 80 weight percent, up to about 70 weight percent, or up to about 60 weight percent intumescent material having an average particle size greater than about 300 micrometers. In some embodiments, the compositions includes about 10 to about 80 weight percent, about 20 to about 70 weight percent, about 30 to about 60 weight percent, or about 40 to about

60 weight percent of the intumescent material having an average particle size greater than about 300 micrometers. The weight percent is based on the dry weight of the composition.

5 For example, the composition can include micaceous binder in an amount of about 5 to about 80 weight percent on a dry weight basis, biosoluble inorganic fibers in an amount of about 5 to about 80 weight percent on a dry weight basis, and intumescent material in an amount of about 10 to about 80 weight percent on a dry weight basis. The micaceous binder can include vermiculite having a particle size less than about 150 micrometers and the intumescent material can include vermiculite having a particle size  
10 greater than about 150 micrometers (none passes through a 100 mesh screen). The intumescent vermiculite can have an average particle size that is greater than about 300 micrometers.

Compositions of the present invention can also include one or more polymeric binders. The polymeric binder can be used to provide added resiliency and flexibility  
15 during formation and during handling of the compositions. For example, when the composition is in the form of sheet material such as a mounting mat for a pollution control device, the mounting mat can be wrapped more easily around the pollution control element. The operating temperatures typically encountered in such a device can break down (e.g., decompose or eliminate) the polymeric constituents. Thus, in some  
20 embodiments, the organic constituents can be transient, rather than permanent, components of the compositions.

Suitable polymeric binders can be thermoplastic or thermoset and can be provided as a 100 percent solids composition, a solution, a dispersion, a latex, an emulsion, combinations of these, and the like. In some embodiments, the polymeric  
25 binder is an elastomer. Suitable polymers include, but are not limited to, natural rubber, copolymers of two or more copolymerizable species including styrene and butadiene, copolymers of two or more copolymerizable species including butadiene and acrylonitrile, (meth)acrylate polymers and copolymers, polyurethanes, polyesters, polyamides, cellulosic polymers, other elastomer polymers, or combinations of these.

30 The compositions can include about 0.1 to about 15 weight percent, about 0.5 to about 12 weight percent, or about 1 to about 10 weight percent of the polymeric binder on a dry weight basis.

In some embodiments, the polymer binders are acrylic- and/or methacrylate-containing latex compositions. Such latex compositions tend to burn cleanly without producing undesirable amounts of toxic or corrosive by-products. Examples of suitable acrylic emulsions include those commercially available under the trade designations

5 "RHOPLEX HA-8" (a 44.5% by weight solids aqueous emulsion of acrylic copolymers) from Rohm and Haas of Philadelphia, PA and under the trade designation "AIRFLEX 600BP" (a 55% solids ethylene vinyl acetate copolymer) from Air Products of Allentown, PA.

Polymeric fibers optionally can be included in the compositions to improve the

10 handling, flexibility, the resiliency, or a combination thereof. When the compositions are in the form of a sheet material, polymeric fibers tend to enhance processing and improve the wet strength of the sheet material. As with the polymeric binder, polymeric fibers tend to burn out (i.e., to decompose or be eliminated) after one or more heating cycles if the compositions are used in a pollution control device.

15 The polymer fibers can be formed from any of the polymers listed above with respect to the polymeric binder. The compositions can include up to about 5 weight percent polymeric fibers on a dry weight basis. In some embodiments, the compositions includes up to about 2 or up to about 1 weight percent polymeric fiber. For example, the compositions can include about 0.1 to about 2 weight percent or about

20 0.2 to about 1.0 weight percent of polymeric fibers on a dry weight basis. The polymeric fibers may be staple fibers or fibrillated fibers. In one embodiment, the polymeric fibers are staple fibers in the range of about 0.5 to about 5 denier.

The compositions can also include other materials in accordance with conventional practices. Such materials include, for example, plasticizers, wetting

25 agents, defoaming agents, latex coagulants, clays, lightweight fillers, refractory fillers, metallic fibers, or combinations of these.

In some embodiments, the compositions are in the form of sheet materials and the sheet materials include an edge protector to minimize erosion to the edges of the sheet material. Such erosion can be caused, for example, by the exhaust gas when the

30 sheet material is used in a pollution control device. Suitable edge protectors can include, for example, a metal mesh placed on the edges of the sheet or a mixture of a binder and glass as disclosed in U.S. Patent No. 6,245,301 (Stroom et al.). Other edge protectors known in the art can be used.

In one embodiment of the present invention, the composition includes about 5 to about 90 weight percent biosoluble inorganic fibers and about 5 to about 80 weight percent micaceous binder on a dry weight basis. For example, the composition can include about 5 to about 80 weight percent micaceous binder and about 5 to about 85 weight percent biosoluble inorganic fibers or about 5 to about 80 weight percent biosoluble inorganic fibers and about 5 to about 80 weight percent biosoluble inorganic fibers.

In other examples, the composition can include about 10 to about 60 weight percent micaceous binder and about 10 to about 60 weight percent biosoluble fibers or about 15 to about 50 weight percent micaceous binder and about 15 to about 40 weight percent biosoluble fibers on a dry weight basis. As yet another example, the composition can include about 15 to about 45 weight percent micaceous binder and about 15 to about 30 weight percent biosoluble fibers on a dry weight basis.

In another embodiment of the present invention, the composition includes, on a dry weight basis, about 5 to about 80 weight percent biosoluble inorganic fibers, about 5 to about 80 weight percent micaceous binder, and about 10 to about 80 weight percent intumescent material having an average particle size greater than about 300 micrometers. For example, the composition can include, on a dry weight basis, about 10 to about 60 weight percent micaceous binder, about 10 to about 60 weight percent biosoluble fibers, and about 20 to about 70 weight percent intumescent material having an average particle size greater than about 300 micrometers.

As another example of this embodiment, the composition can include, on a dry weight basis, about 15 to about 50 weight percent micaceous binder, about 15 to about 40 weight percent biosoluble fibers, and about 30 to about 60 weight percent intumescent material having an average particle size greater than about 300 micrometers. As yet another example, the composition can include, on a dry weight basis, about 15 to about 45 weight percent micaceous binder, about 15 to about 30 weight percent biosoluble fibers, and about 40 to about 60 weight percent intumescent material having an average particle size greater than about 300 micrometers.

In another embodiment, the composition includes about 5 to about 80 weight percent biosoluble inorganic fibers, about 5 to about 80 weight percent micaceous binder, about 10 to about 80 weight percent intumescent material having an average

particle size greater than about 300 micrometers, and up to about 15 weight percent polymeric binder on a dry weight basis.

For example, the composition according to this embodiment can include about 15 to about 50 weight percent micaceous binder, about 15 to about 40 weight percent biosoluble fibers, about 40 to about 60 weight percent intumescent material having an average particle size greater than about 300 micrometers, and about 0.5 to about 12 weight percent polymeric binder on a dry weight basis.

In yet another embodiment, the composition can include about 5 to about 80 weight percent biosoluble inorganic fibers, about 5 to about 80 weight percent micaceous binder, about 10 to about 80 weight percent intumescent material having an average particle size greater than about 300 micrometers, up to about 15 weight percent polymeric binder, and up to about 5 weight percent polymeric fibers on a dry weight basis.

For example, the composition according to this embodiment can include about 15 to about 50 weight percent micaceous binder, about 15 to about 40 weight percent biosoluble fibers, about 40 to about 60 weight percent intumescent material having an average particle size greater than about 300 micrometers, about 0.5 to about 12 weight percent polymeric binder, and up to about 2 weight percent polymeric fiber on a dry weight basis.

Sheet materials prepared from the compositions of the present invention can have a single layered or multilayered construction. In one embodiment, the sheet material can include a first layer having biosoluble inorganic fibers and a micaceous binder and at least one additional layer provided on this first layer. A representative embodiment of such an additional layer can include, but is not limited to, ingredients such as glass fibers as disclosed in U.S. Patent No. 5,290,522 (Rogers et al.), shot free ceramic fibers as disclosed in U.S. Patent No. 4,929,429 (Merry), an intumescent material, or a combination thereof.

For example, the multilayered sheet material can include a first layer that contains biosoluble inorganic fiber and a micaceous binder and a second layer that contains fibers capable of withstanding high temperatures. Fibers capable of withstanding high temperatures include, but are not limited to, fibers sold under the trade designation "SAFFIL" by Saffil Limited (Pilkington, U.K) and fibers sold under the trade designation "NEXTEL" by 3M (St. Paul, MN).

The multilayered sheet material can be formed using any of a variety of conventional fabrication techniques. One representative fabrication approach involves forming individual layers and then laminating the layers together using an adhesive.

5 Multilayer sheet material can also be formed as described in U.S. Patent No. 5,853,675 (Howorth). Alternatively, the layers can be formed one on top of the other as described in U.S. Patent No. 6,051,193 (Langer et al.).

The sheet materials prepared from the compositions of the present invention can be formed using any of a variety of suitable techniques such as, for example, a papermaking process. In one embodiment of a papermaking approach, a micaceous  
10 binder is prepared by adding expanded micaceous mineral(s) to water. The concentration and temperature can both vary over a wide range. In some embodiments, warm water, such as water at a temperature of about 30 °C to about 75 °C, can be used to prepare the slurry. For example, the water can be at a temperature of about 35 °C to about 45 °C. The mineral is delaminated (i.e., exfoliated) and crushed to a particle size  
15 suitable for a binder (i.e., less than about 150 micrometers).

A dilute slurry can be prepared by adding water to the micaceous binder. Biosoluble inorganic fibers and optionally other inorganic and polymeric fiber constituents can be added to the slurry. Any amount of shear that disperses the micaceous binder and biosoluble fibers can be used. In some embodiments, low to  
20 moderate shear for a relatively brief time, e.g., 1 second to 10 minutes or about 3 to 80 seconds, can be used to disperse the fibers. The slurry can be mixed at moderate speed to keep the solid ingredients suspended. Other ingredients such as a defoaming agent and polymeric binders can be added.

A suitable coagulating agent such as an acidifying agent can be added. Other  
25 coagulating agents, such as one that can cause coagulation via basic means, can also be used in accordance with conventional practices. During coagulation, larger particles of the polymeric binder typically formed. The fines and other particulate matter tend to be bound to the polymeric binder and trapped in the fiber matrix. That is, the fines do not cause clogging of screens used for filtering. Binding the fines to the fiber matrix  
30 facilitates draining the water from the slurry and can decrease the processing time needed to prepare sheet material.

The optional intumescent material having an average particle size greater than about 300 micrometers is typically added after coagulation. This particular order of

addition can also facilitate dispersing the solids in the slurry and removing the water from the slurry. However, the order of addition is not critical and other orders of addition are acceptable.

5 The resultant slurry composition can be cast onto a suitable screen, drained, and pressed. Alternatively, the plies can be formed by vacuum casting the slurry onto a wire mesh or screen. The resultant pressed sheet material can be dried in any suitable manner, e.g., air dried or oven dried. For a more detailed description of the standard paper making techniques employed, see U.S. Pat. No. 3,458,329 (Owens et al.).

10 The sheet material can be cut into a desired shape such as a shape suitable for use as a mounting mat or for use as a heat barrier (i.e., insulating material) in the end-cone region of a pollution control device. Cutting can be accomplished, for example, by using a die stamping process. The sheet materials prepared from the compositions of the invention can be reproducibly cut to satisfy stringent size tolerances. The sheet materials can exhibit suitable handling properties and are not so brittle as to crumble in one's hand. For example, the sheet materials can be easily and flexibly fitted around a pollution control element without breaking apart to form a resilient, protective, supportive seal in a pollution control device.

15 The compositions of the invention can also be prepared in the form of a paste. To prepare a paste, the total solids are typically higher than about 30 percent. In some embodiments, the solids are about 30 to about 60 percent. The paste typically has a consistency and viscosity that can be injected, for example, into the gap between a pollution control element and the housing of a pollution control device. U.S. Patent No. 5,736,109 (Howorth), describes a suitable process for making a paste. A paste can also be formed by initially forming a slurry and then removing some of the water to increase the percent solids. Further, the paste can be used to form a sheet material.

25 Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. All parts and percentages are by weight unless stated otherwise.

30

### EXAMPLES

The following tests were used to characterize the sheet material included in the examples and comparative examples.

**Elevated Temperature Shrinkage**

This test was used to determine the shrinkage of sheet material at temperatures that may be seen in a pollution control device. A sample was cut from a sheet using a square die having dimensions of 4.44 cm by 4.44 cm. The sample was measured in the X-Y plane using a dial caliper gauge to determine the area ( $A_{\text{before heating}}$ ), and then placed in a Thermalayne Type 48000 furnace that had been pre-heated to 900°C. The sample was heated for 24 hours, 48 hours, or 72 hours as indicated in the test results. After removal from the furnace, the sample was cooled to room temperature and measured with the caliper gauge to determine the area after heating ( $A_{\text{after heating}}$ ). The percent shrinkage (% Shrinkage) was determined as follows.

$$\% \text{ Shrinkage} = [(A_{\text{before heating}} - A_{\text{after heating}}) / A_{\text{before heating}}] \times 100$$

The sheet material may expand in the Z-axis as a consequence of heating, but this kind of expansion was disregarded in determining percent shrinkage per the above formula. The shrinkage of sheet materials of the present invention is typically less than about 6 percent. Typical mounting mats used in the industry have shrinkage of about 4 percent to about 5 percent.

**Real Condition Fixture Test (RCFT)**

This test was used to measure the pressure exerted by the sheet material under conditions representative of actual conditions found in a pollution control element such as a catalytic converter during normal use. Details are further described in U.S. Patent No. 5,869,010.

A sheet material sample having dimensions of 4.44 cm by 4.44 cm was placed between two 50.8 mm by 50.8 mm heated, metal platens having independent heating controls. Each platen was heated incrementally to a different temperature profile to simulate the temperatures of the metal housing and the monolith in a catalytic converter. During heating, the gap between the platens was increased by a value calculated from the temperatures and thermal expansion coefficients of a typical catalytic converter housing and monolith. After heating to the maximum temperature,



the platens were cooled incrementally and the gap was decreased by a value calculated from the temperatures and thermal expansion coefficients.

5 The materials are initially compressed to a selected density to simulate protective packing material in a pollution control device. This initial density, typically ranging from about 0.80 to about 1.0 g/cc, is referred to as the mount density.

10 The force exerted by the mounting material was measured using a Sintech ID computer controlled load frame with an Extensiometer (available from MTS Systems Corp., Research Triangle Park, NC. The pressure exerted by the mat during the heating and cooling cycle was plotted against the temperature profile. The sample and platens were cooled to room temperature, and the cycle was repeated two more times to produce a graph having 3 plots of pressure vs. temperature. A minimum value of at least 50 kiloPascals (kPa) for each of the three cycles is typically considered desirable. However, if a lower pressure was observed at some point on a plot, the mat may still be suitable.

15

#### **Examples 1-3 and Comparative Example C1**

20 Sheet materials were prepared by adding 1500 ml of tap water at 40°C and expanded vermiculite (ZONELITE Expanded Vermiculite #5 obtained from W.R. Grace, Cambridge, MA) to a Waring blender. The blender was run on the low setting for 3 minutes to delaminate and crush the vermiculite. Then Fraunhofer certified biosoluble inorganic fibers (SUPERWOOL 607 available from Thermal Ceramics, Augusta GA) were added and blended on low for 3 seconds. The amounts of expanded vermiculite and biosoluble inorganic fibers totaled 25 grams and specifics are shown in Table 1.

25 The blender contents were poured into a stainless steel container and 2000 ml of water at 40°C were used to rinse out the blender and the contents were added to the stainless steel container. The contents of the container and 3 drops of a defoamer (FOAMMASTER III available from Henkel) were mixed using a propeller mixer at medium speed to keep the solids suspended. A 55 percent solids ethylene vinyl acetate copolymer latex (AIRFLEX 600BP available from Air Products Polymers Allentown, PA) was added in the amounts shown and mixed for 1 minute. Then 20 grams of a 25 percent solids solution of aluminum sulfate (Aluminum Sulfate Solution available from Koch Sulphur Products of Pinebend, MN) were added to coagulate the latex.

30

The resulting slurry was poured into a handsheet former and drained. The resulting sheet was covered with blotting paper. After rolling with a rolling pin 3 times, the sheet was placed between blotting papers and pressed for 5 minutes and 552 kiloPascals, and then dried for 15 minutes in a convection oven set at 150°C. The sheet was conditioned at room temperature (approximately 22°C) and tested for shrinkage according to the above procedure.

Comparative Example C1 was prepared in the same manner except that no expanded vermiculite was used.

Table 1				
	Ex 1	Ex 2	Ex 3	Ex C1
Expanded vermiculite – grams	20.9	4.0	12.5	0
Soluble Fibers –grams	4.1	21.0	12.5	25
Latex-grams	6.0	7.0	7.4	7.1
Dry mat composition				
Expanded vermiculite - %	74	13.8	43	0
Soluble Fibers - %	14.4	72.7	43	86.5
Latex - %	11.7	13.5	14	13.5
% Shrinkage	0.2	2.0	1.9	7.0

The data in Table 1 show that sheet materials of the invention exhibit significantly less shrinkage than compositions having only soluble fibers.

#### **Example 4 and Comparative Examples C2-C3**

An intumescent mat composition was prepared using the procedure described for Example 1 and the compositions shown in Table 2. The biosoluble inorganic fibers were blended for about 5 seconds before adding the latex, and 10 parts of a 50 percent solids solution of aluminum sulfate were added to coagulate the latex. The unexpanded vermiculite was vermiculite ore obtained from Cometals, Inc. New York, NY and had a mesh size less than 18 mesh (less than about 1mm in size). The unexpanded vermiculite was added after coagulating the latex and mixed to form a fairly uniform dispersion.

Example C2 was prepared as Example 4 except without expanded vermiculite.

The sheet materials were tested for shrinkage after heating at 900°C for 25 hours and 72 hours. The results are shown in Table 2.

Table 2				
	Ex 4 Composition		Ex C2 Composition	
	Wet-grams	Dry-%	Wet-grams	Dry-%
Expanded vermiculite	25	22	0	0
Soluble Fibers	25	22	50	44
Unexpanded vermiculite	55	49	55	49
Latex	15	7	15	7
% Shrinkage after 24 hrs	0.7		10.8	
% Shrinkage after 72 hrs	3.9		16.3	

5

The data in Table 2 show that an intumescent sheet materials of the invention shrinks considerably less than a mat of the same composition without the expanded, delaminated, and crushed vermiculite binder.

Example 4 was then tested in the real condition fixture test (RCFT). The mount density was 0.90 g/cc. The sample was held at peak temperature for 2 hours. The are shown in Figure 3. The first cycle is shown in plot 2, the second cycle is shown in plot 3, and the third cycle is shown in plot 1. The pressure was above 50 kPa during all three cycles at all temperatures, indicating that the mat is suitable for use in a catalytic converter.

15

#### **Example 5**

A sheet material was prepared as in Example 4 except that the expanded vermiculite was Micron Grade Expanded Vermiculite obtained from The Strong Co., Inc., Pine Bluff, AR, and 1 gram of 0.635 long rayon fibers (available from Minifibers Inc Johnson City, TN) was added to the slurry with the soluble fibers. A graph of the results is shown in Figure 4. The mount density was 0.95 g/cc. The sample was held at the peak temperature for 2 hours. The first cycle is shown in plot 4, the second cycle is shown in plot 5, and the third cycle is shown in plot 6. The intumescent mat had acceptable shrinkage and pressures above 100 kPa when tested in the RCFT.

20

### Example 6

A multilayered construction was formed from a layer of dry-laid and needle punched sheet made as described in patent US 5,290,522 (Rogers, et al.) at about 700  
5 grams per square meter and a layer of intumescent sheet of Example 5 at about 2770 grams per square meter. The two layers were placed together, and the construction was tested in the RCFT (real condition fixture test) with the Example 5 layer placed next to the hot side platen and the dry-laid sheet placed next to the cold side platen. When  
10 tested for three temperature cycles as described in Example 5 at a mount density of about 0.7 grams per cubic centimeter but with the maximum platen temperature reaching only 500°C on the hot platen and 200°C on the cold platen, a minimum pressure of about 75 kilopascals and a maximum pressure of about 220 kilopascals was observed. These results demonstrate the general utility of using layered constructions of the present invention as mounting systems in a variety of applications.

### Example 7

A sample was prepared containing unexpanded vermiculite as the micaceous binder. The sheet material was prepared using 45 weight percent unexpanded vermiculite, 45 weight percent SUPERWOOL 607, and 15 weight percent AIRFLEX  
20 600BP latex.

The unexpanded vermiculite was obtained from a vermiculite ore, available from Cometal, Inc, of New York, NY. The vermiculite ore was screened such that the fraction that passed through a 20 mesh screen but not a 50 mesh screen was collected. 54 grams of 20-50 mesh fraction of the vermiculite ore and 1500 ml tap water  
25 conditioned to 40 °C were added to a Waring Blender and mixed at low speed for 3 minutes. The vermiculite slurry was then mixed for an additional 3 minutes at high speed in 1 minute increments, allowing the blender motor to cool 3-5 between operations. 54 grams of SUPERWOOL 607 and 1000 conditioned tap water were then added to the blender and mixed for 3 to 5 seconds. The slurry was then transferred to a  
30 mixing vessel and the blender was rinsed with 1000 ml conditioned tap water to remove any remaining solids from the blender.

The slurry was then suspended and mixed with a paddle mixer at medium speed and 3 drops FOAMMASTER 111 defoamer added. 21.82 grams AIRFLEX 600BP

latex was then added and allowed to disperse for 2-3 minutes. 10 grams of 50% alum solution was then added to precipitate the mix.

The precipitated mixture was then poured into a 8 in. by 8 in. handsheet mold having a 60 mesh screen. The water was drained from the mold to form a handsheet.

5 The handsheet was then rolled under blotter paper with a rolling pin to remove excess water and pressed at 35 psi for 5 minutes between to 40 mesh screens on metal frames and dried in a 150 °C convection oven.

After equilibrating to room temperature and humidity overnight, a 1-3/4 in. by 1-3/4 in. sample was die cut from the handsheet for testing.

10 The die cut sample dimensions were measured in the x-y plane using a dial micrometer and then placed in a small muffle furnace set at 1000 degrees C for 48 hrs. After cooling, the sample dimensions were again measured in the x-y plane. The area before and after heating as well as percent shrinkage were calculated from the micrometer measurements. The shrinkage was 4.3 percent.

15 Other embodiments of this invention will be apparent to those skilled in the art upon consideration of this specification or from practice of the invention disclosed herein. Various omissions, modifications, and changes to the principles and embodiments described herein may be made by one skilled in the art without departing  
20 from the true scope and spirit of the invention which is indicated by the following claims.

## WHAT IS CLAIMED IS:

1. A composition comprising:
  - a) a micaceous binder in an amount of about 5 to about 80 weight percent on a dry weight basis; and
  - b) biosoluble inorganic fibers in an amount of about 5 to about 90 weight percent on a dry weight basis.
2. The composition of claim 1, wherein said composition is in the form of a paste or a sheet material.
3. The composition of claim 1, wherein the composition is in a form suitable for use in a pollution control device.
4. The composition of claim 1, wherein the composition is in a form suitable for use as a mounting mat of the pollution control device.
5. The composition of claim 3, wherein the composition is in a form suitable for use as an insulating material in an end cone region of a pollution control device.
6. The composition of claim 1, wherein said composition is in a form suitable for use as a heat barrier, a fire barrier, or as a protective packing material.
7. The composition of claim 1, wherein the composition is in the form of a sheet material having an area in a X-Y plane, the area decreasing less than about 6 percent when said sheet material is heated to about 900 °C.
8. The composition of claim 1, wherein said biosoluble inorganic fibers comprise about 45 to about 90 weight percent SiO<sub>2</sub>, up to about 45 weight percent CaO, up to about 35 weight percent MgO, and less than 10 weight percent Al<sub>2</sub>O<sub>3</sub> based on the weight of the biosoluble inorganic fibers.

9. The composition of claim 1, wherein said micaceous binder comprises a micaceous mineral having a particle size less than about 150 micrometers.
- 5 10. The composition of claim 9, wherein said micaceous mineral comprises vermiculite.
11. The composition of claim 10, wherein the vermiculite is non-intumescent.
- 10 12. The composition of claim 1, further comprising non-respirable inorganic fiber in an amount up to about 15 weight on a dry weight basis.
- 15 13. The composition of claim 1, further comprising an intumescent material in an amount up to about 80 weight percent on a dry weight basis, wherein said intumescent material has an average particle size greater than about 300 micrometers.
- 20 14. The composition of claim 1, further comprising an intumescent material in an amount up to about 80 weight percent on a dry weight basis, wherein said intumescent material comprises a micaceous mineral having a particle size greater than about 150 micrometers.
- 25 15. The composition of claim 14, wherein said intumescent material comprises unexpanded vermiculite.
16. The composition of claim 1, further comprising a polymeric binder in an amount of about 0.1 to about 15 weight percent on a dry weight basis.
17. The composition of claim 16, wherein said polymeric binder is an elastomer.
- 30 18. The composition of claim 1, further comprising polymeric fibers.
19. The composition of claim 1, wherein said composition is in the form of a sheet material having a multilayered construction.

20. The composition of claim 2, wherein said sheet material further comprises an edge protector.
- 5 21. The composition of claim 1, wherein said composition is free of respirable inorganic fibers that are durable.
22. A composition comprising:
- 10 a) a micaceous binder in an amount of about 15 to about 50 weight percent on a dry weight basis, wherein the micaceous binder comprise vermiculite having a particle size less than about 150 micrometers;
- b) biosoluble inorganic fibers in an amount of about 15 to about 40 weight percent on a dry weight basis; and
- 15 c) intumescent material in an amount of about 30 to about 60 weight percent on a dry weight basis, wherein the intumescent material comprises unexpanded vermiculite having a particle size greater than about 150 micrometers.
23. The composition claim 22, further comprising a polymeric binder in an amount of about 0.1 to about 15 weight percent on a dry weight basis.
- 20 24. A pollution control device comprising:
- a) a housing;
- b) a pollution control element disposed in the housing; and
- 25 c) a protective material disposed in a gap between at least a portion of the housing and a portion of the pollution control element, said a protective material comprising:
- i) a micaceous binder; and
- 30 ii) biosoluble inorganic fibers.
25. The pollution control device of claim 24, wherein the protective material is in the form of a sheet material or a paste.



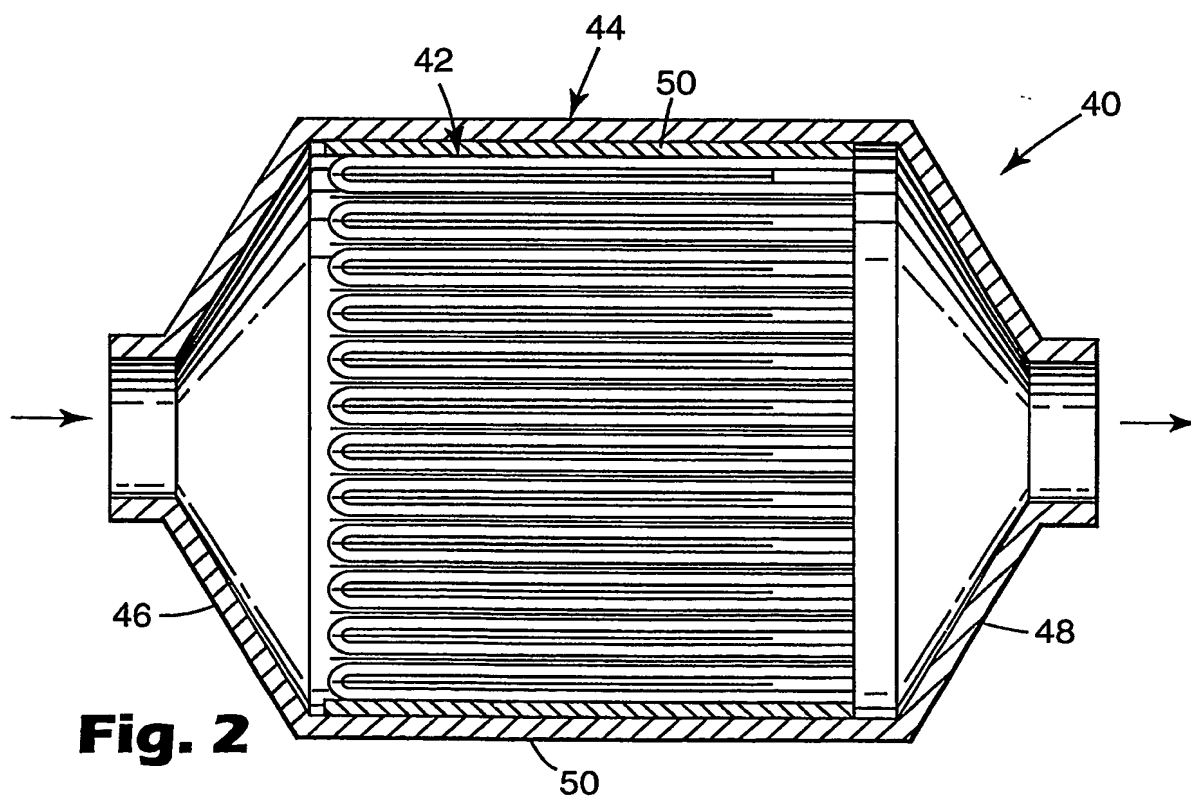
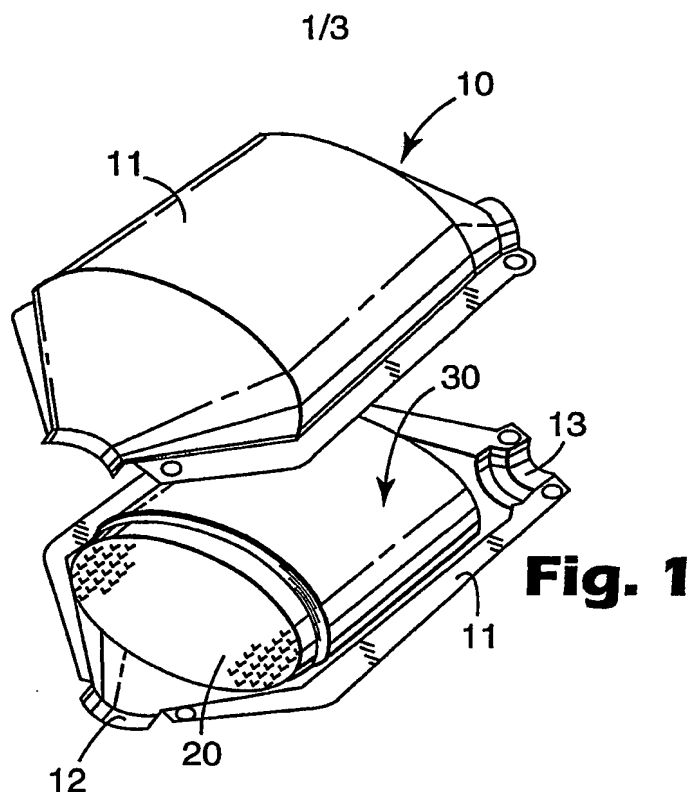
- 5 26. The pollution control device of claim 24, wherein said a protective material comprises micaceous binder in an amount of about 5 to about 80 weight percent on a dry weight basis and biosoluble inorganic fibers in an amount of about 5 to about 90 weight percent on a dry weight basis.
- 10 27. The pollution control device of claim 24, wherein said biosoluble inorganic fibers comprise about 45 to about 90 weight percent  $\text{SiO}_2$ , up to about 45 weight percent  $\text{CaO}$ , up to about 35 weight percent  $\text{MgO}$ , and less than 10 weight percent  $\text{Al}_2\text{O}_3$  based on the weight of the biosoluble inorganic fibers.
- 15 28. The pollution control device of claim 24, wherein said micaceous binder comprises vermiculite having a particle size less than about 150 micrometers.
- 20 29. The pollution control device of claim 24, wherein said a protective material further comprises an intumescent material in an amount up to about 80 weight percent on a dry weight basis, wherein said intumescent materials has an average particle size greater than about 300 micrometers.
- 25 30. The pollution control device of claim 24, wherein said a protective material further comprises non-respirable inorganic fibers in an amount up to about 15 weight percent on a dry weight basis.
- 30 31. The pollution control device of claim 24, wherein said a protective material comprises a sheet material having an area in an X-Y plane, said area decreasing less than about 6 percent when said pollution control device is in use.
32. A pollution control device comprising a housing and insulating material disposed in said housing, said insulting material comprising a micaceous binder and biosoluble fibers.
33. The pollution control device of claim 32, wherein the insulating material is in an end cone region of the housing.

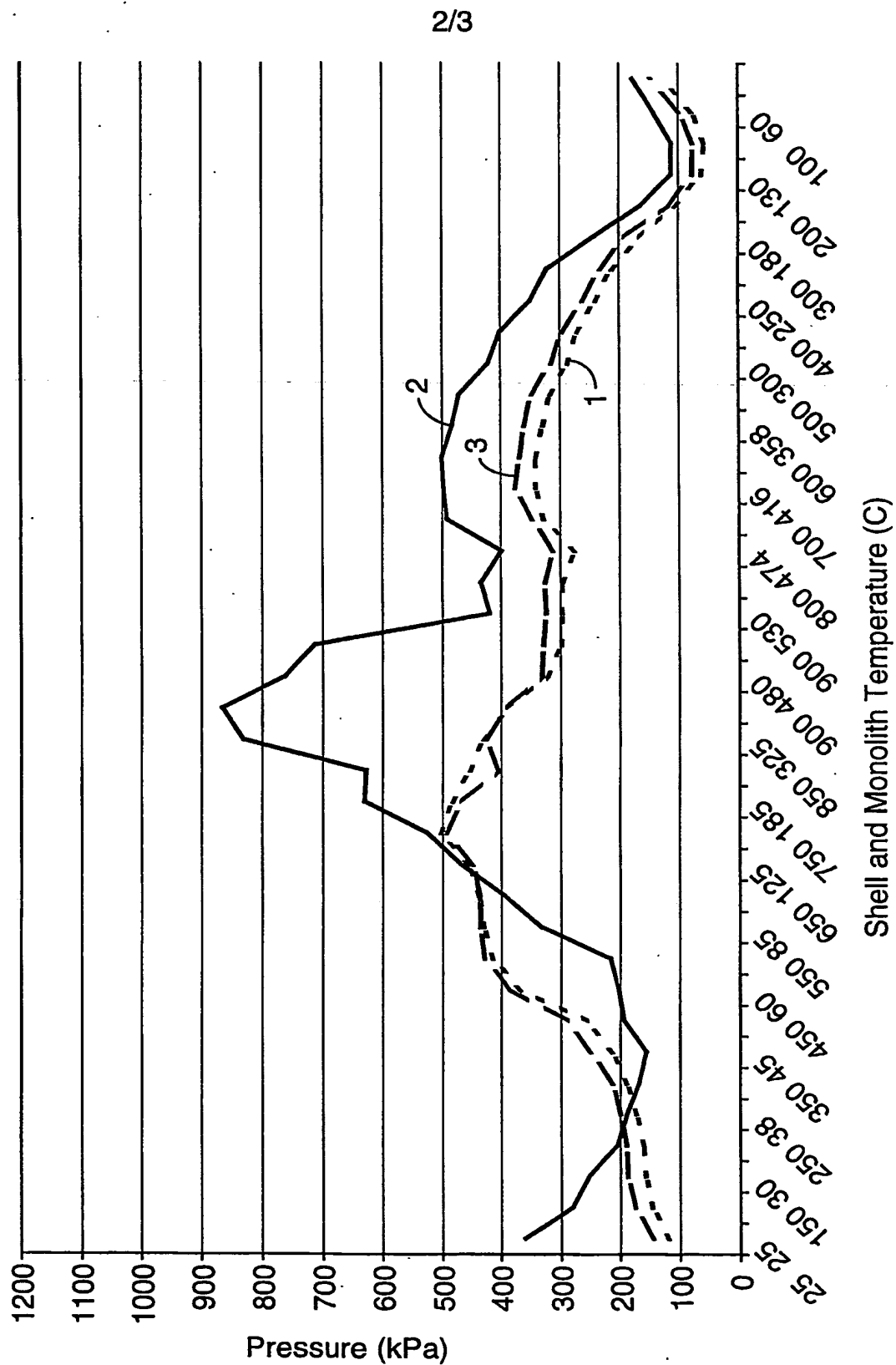
34. The pollution control device of claim 32, wherein said insulating material comprises micaceous binder in an amount of about 5 to about 80 weight percent on a dry weight basis and biosoluble inorganic fibers in an amount of about 5 to about 90 weight percent on a dry weight basis.
35. A sheet material comprising a mixture of a micaceous binder and biosoluble inorganic fibers, wherein said sheet material has an area in a X-Y plane, wherein the area decrease less than about 6 percent when said sheet material is heated to about 900 °C.
36. The sheet material of claim 35, wherein sheet material comprises the micaceous binder in an amount of about 5 to about 90 weight percent and biosoluble inorganic fibers in an amount of about 5 to about 80 weight percent.
37. A method of making a pollution control device comprising  
providing a housing and a pollution control element;  
forming a protective packing material comprising a micaceous binder and biosoluble inorganic fibers;  
disposing the pollution control element in the housing; and  
positioning the protective packing material between at least of portion of pollution control element and the housing.
38. The method of claim 37, wherein the protective packing material is in the form of a sheet material and the sheet material is wrapped around at least a portion of the pollution control device.
39. The method of claim 37, wherein the sheet material further comprises an intumescent material having an average particle size greater than about 300 micrometers.
40. A method of making a sheet material comprising:

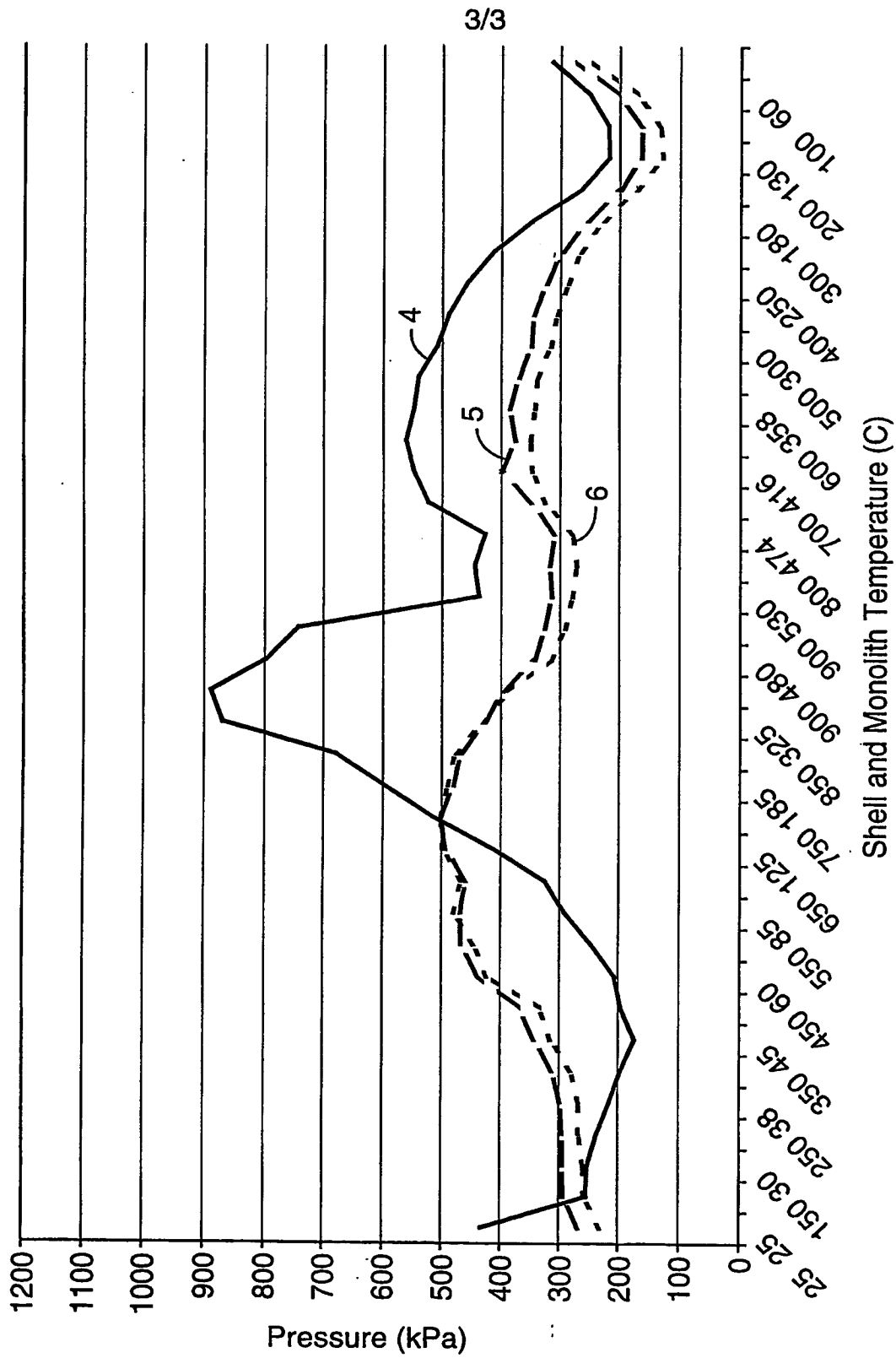
forming an aqueous slurry comprising a micaceous binder in an amount of about 5 weight percent to about 80 weight percent on a dry weight basis and biosoluble inorganic fibers in an amount of about 5 to about 90 weight percent on a dry weight basis;

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adding a coagulating agent to form a coagulated slurry; and  
removing water from the coagulated slurry to form a sheet material.







**Fig. 4**

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(71) Applicant (for all designated States except US): **3M IN-  
NOVATIVE PROPERTIES COMPANY** [US/US]; 3M  
Center, Post Office Box 33427, Saint Paul, MN 55133-  
3427 (US).

(72) Inventor; and

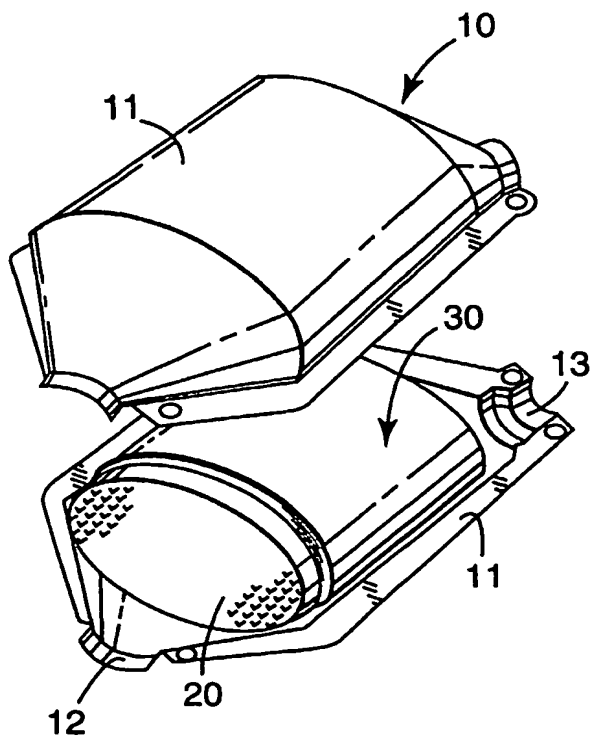
(75) Inventor/Applicant (for US only): **HOWORTH, Gary, F.**

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[Continued on next page]

(54) Title: COMPOSITIONS CONTAINING BIOSOLUBLE INORGANIC FIBERS AND MICACEOUS BINDERS



(57) Abstract: Compositions that include a mixture of biosoluble inorganic fibers and a micaceous binder are described. The compositions can be prepared free of refractory ceramic fibers that are respirable but durable in a physiological medium. The compositions are typically in the form of a sheet material or a paste and can be used, for example, as a protective packing material around the pollution control element or as an insulating material in the end cone region in a pollution control device. Sheet materials formed from the compositions have an area of a X-Y plane that decrease less than about 6 percent when heated to about 900°C.



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## B. FIELDS SEARCHED

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## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 02219 A (MINNESOTA MINING & MFG) 23 January 1997 (1997-01-23)  page 4, line 24 - line 31 page 5, line 25 - page 6, line 28 page 11, lines 6-12; claims 1,10	1-6,12, 13,16, 18,22, 26,30, 32,34, 37,40
A		1-6,10, 13-18
A	EP 0 739 862 A (SCHULLER INT INC) 30 October 1996 (1996-10-30)  claims	1,8,22, 24,27, 32,34
	-/--	

☒ Further documents are listed in the continuation of box C.

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European Patent Office, P.B. 6818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl  
Fax: (+31-70) 340-3016

Authorized officer

Theodoridou, E.

## INTERNATIONAL SEARCH REPORT

International Application No  
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 714 421 A (KIELMEYER WILLIAM HENRY ET AL) 3 February 1998 (1998-02-03) cited in the application  column 1, line 26 - column 2, line 63; claims	1,2,6,8, 10,13, 15,16, 18,40
Y	GB 2 220 936 A (DIDIER WERKE AG) 24 January 1990 (1990-01-24)  page 1, lines 4-12,25-30 page 2, line 16 - page 3, line 32	1,2,6,8, 10,13, 15,16, 18,40
A	US 2001 024626 A1 (TENNEYCK JOHN D) 27 September 2001 (2001-09-27)  paragraphs '0014!, '0023!, '0025!, '0027!, '0032!	1-5,8, 16, 24-27, 37,38
A	DATABASE CHEMABS 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; LUKASIK, JERZY ET AL: "Superwool fiber proposed by the Thermal Ceramics company for reducing harmful effect of foundries on environment" XP002244589 retrieved from STN Database accession no. 134:104483 abstract & NOWOCZESNE TECHNOLOGIE ODLEWNICZE--OCHRONA SRODOWISKA, MIEDZYNARODOWA KONFERENCJA, 3RD, KRAKOW, POLAND, SEPT. 7-9, 2000 (2000), MEETING DATE 2000, 223-227 PUBLISHER: AKADEMIA GORNICZO-HUTNICZA IM. STANISLAWA STASZICA, WYDZIAL ODLEWNICTWA, KRAKOW, POL. CODEN: 69AOLM,	1,8,24, 27
A	US 5 705 444 A (TOMPKINS THOMAS L ET AL) 6 January 1998 (1998-01-06) claims	1-6,22
A	US 4 385 135 A (MARLOR ALAN J ET AL) 24 May 1983 (1983-05-24) cited in the application claims	1,2, 9-11,14, 15,40

## INTERNATIONAL SEARCH REPORT

International	Application No
PCT/US	02/32350

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9702219	A	23-01-1997	AU 5804396 A	05-02-1997
			BR 9609516 A	23-02-1999
			CA 2224325 A1	23-01-1997
			DE 69604922 D1	02-12-1999
			DE 69604922 T2	15-06-2000
			EP 0835230 A1	15-04-1998
			JP 11509510 T	24-08-1999
			WO 9702219 A1	23-01-1997
			US 5869010 A	09-02-1999
EP 0739862	A	30-10-1996	US 5401693 A	28-03-1995
			EP 0739862 A2	30-10-1996
			AT 151061 T	15-04-1997
			CA 2106412 A1	19-03-1994
			DE 69309374 D1	07-05-1997
			DE 69309374 T2	23-10-1997
			DK 588251 T3	29-09-1997
			EP 0588251 A1	23-03-1994
			JP 2588360 B2	05-03-1997
			JP 6321578 A	22-11-1994
			US 5981414 A	09-11-1999
US 5714421	A	03-02-1998	US 5332699 A	26-07-1994
			AU 3765789 A	05-01-1990
			CA 1338340 C	21-05-1996
			WO 8912032 A2	14-12-1989
			AU 590393 B2	02-11-1989
			AU 6948887 A	09-09-1987
			BR 8706031 A	19-01-1988
			CA 1271785 A1	17-07-1990
			DK 545387 A	19-10-1987
			EP 0257092 A1	02-03-1988
			ES 2003226 A6	16-10-1988
			FI 874620 A ,B	20-10-1987
			IN 169752 A1	21-12-1991
			JP 7042139 B	10-05-1995
			KR 9100197 B1	23-01-1991
			NO 874323 A ,B,	16-10-1987
			NZ 219302 A	27-09-1989
			PT 84326 A ,B	01-03-1987
			WO 8705007 A1	27-08-1987
			IN 166538 A1	26-05-1990
			JP 63502746 T	13-10-1988
			MX 162165 A	04-04-1991
GB 2220936	A	24-01-1990	DE 3824472 A1	25-01-1990
			FR 2634479 A1	26-01-1990
			IT 1231623 B	18-12-1991
			JP 2074575 A	14-03-1990
			SE 468210 B	23-11-1992
			SE 8902543 A	20-01-1990
US 2001024626	A1	27-09-2001	US 6231818 B1	15-05-2001
			BR 9915039 A	17-07-2001
			CA 2353566 A1	15-06-2000
			CN 1329517 T	02-01-2002
			DE 1165209 T1	04-07-2002
			EP 1165209 A1	02-01-2002

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 02/32350

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2001024626 A1		HU 0104490 A2 JP 2002531720 T WO 0033946 A1	28-03-2002 24-09-2002 15-06-2000
US 5705444 A	06-01-1998	AU 709950 B2 AU 6898396 A BR 9612604 A CA 2252836 A1 DE 69612121 D1 DE 69612121 T2 EP 0914186 A1 JP 2001526581 T WO 9741942 A1	09-09-1999 26-11-1997 29-06-1999 13-11-1997 19-04-2001 25-10-2001 12-05-1999 18-12-2001 13-11-1997
US 4385135 A	24-05-1983	AU 560556 B2 AU 1496283 A CA 1176451 A1 DE 3366721 D1 EP 0095308 A1 JP 1024750 B JP 1539342 C JP 58213691 A	09-04-1987 01-12-1983 23-10-1984 13-11-1986 30-11-1983 12-05-1989 16-01-1990 12-12-1983